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Methyl 2,3-amino-3-*N*,4-*O*-carbonyl-2,3-*N*-*cyclo*-2,3,6-trideoxy-β-L-allopyranoside

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.082
Data-to-parameter ratio = 9.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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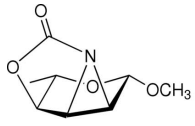
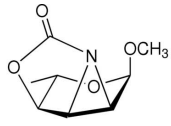
In the structure of the title compound, $C_8H_{11}NO_4$, the aziridine and oxazolidinone rings induce flattening of the pyranoside ring, resulting in five of the six pyranoside ring atoms being nearly coplanar. The pyranoside ring thus adopts an E_5 conformation, the methyl and methoxy substituents both being pseudo-axially disposed.

Comment

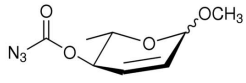
The title compound, (I), was prepared, together with its α-isomer (II) upon photolysis of acylazide (III) with 254 nm light in dichloromethane. Both (I) and (II) are key intermediates in a new route (Mendlik, Tao *et al.*, 2006) for the preparation of glycosides of ristosamine (IV), an aminosugar that is found in a number of natural products including the ristomycins, members of the vancomycin antibiotic family (Crowley *et al.*, 2004). Differentiating (I) and (II) by NMR spectroscopy was impossible and thus both were crystallized and subjected to single-crystal X-ray analysis. The structure of (II) is reported separately (Mendlik, Coleman *et al.*, 2006).



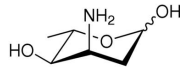
(I)



(II)



(III)



(IV)

The molecular structure of (I) is shown in Fig. 1. Not unsurprisingly, the fusion of the aziridine and oxazolidinone rings to the pyranoside ring flattens it such that five of the six ring atoms (C1/C2/C3/C4/O1) are roughly coplanar [within 0.0823 (12) Å of the least-squares plane], with atom C5 displaced 0.634 (2) Å from this plane (Fig. 2). The pyranoside ring in (I) therefore adopts an E_5 conformation, the polar coordinates being $d = 1.02$, $\varphi = 64^\circ$ and $\theta = 149^\circ$ (Berces *et al.*, 2001). In this conformation, the two pyranoside substituents that are not part of the aziridine or oxazolidinone rings, the methyl group at C5 and the methoxy group at C1, are projected pseudo-axially. This is the preferred disposition for the methoxy group as it allows for stabilization of the molecule *via* the anomeric effect (Lemieux & Koto, 1974). In contrast, the pseudo-axial orientation of the methyl group would not, at first glance, appear to be favored. However, the flattened pyranoside ring structure mitigates any unfavorable 1,3-diaxial interactions as H3 is pseudo-equatorial, not pseudo-axial. Moreover, flattening of the pyranoside ring also increases the distance between this methyl group and the methoxy group at C1 thus reducing any negative steric interactions between these substituents. As is usual in crystal

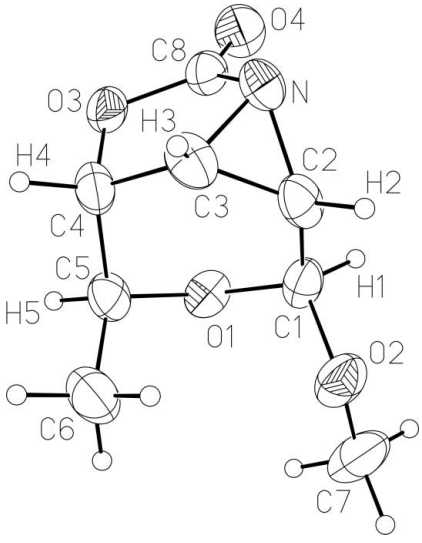


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms as small spheres.

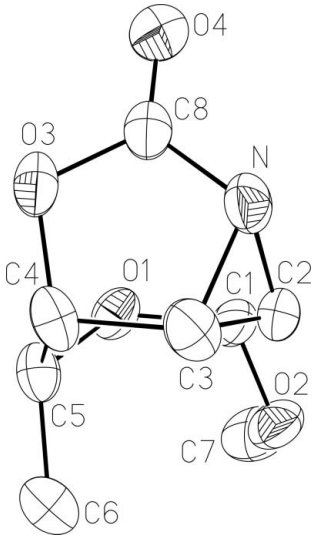


Figure 2
View of (I) illustratiing of the flattening of the pyranoside ring. Displacement ellipsoids are drawn at the 50% probability level. H atoms are not shown.

structures of glycosides, the rotamer about the C1—O2 bond that is present is the one in which O2 is *anti* to C2 and *gauche* to the pyranoside ring O atom as this is the rotamer favored by the *exo*-anomeric effect (Lemieux & Koto, 1974).

In the aziridine ring, the C—N bonds are of unequal length; the C2—N bond is slightly longer than the C3—N– bond, 1.502 (2) *versus* 1.476 (2) Å, respectively. In the rigid tricyclic ring system, the oxazolidinone is forced out of its preferred planar geometry, the N—C3—C4—O3 angle being −13.38 (18)°.

Experimental

Methyl 4-*O*-azidocarbonyl-2,3,6-trideoxy-α/β-L-*erythro*-hex-2-eno-pyranoside (1.496 g, 7.02 mmol), (III) (Mendlik, Tao *et al.*, 2006), was dissolved in CH_2Cl_2 (702 ml, 0.01 *M*). In 150 ml portions, the reaction mixture was exposed to 254 nm light at room temperature in a quartz vessel for 1 h. The reaction mixtures were combined, concentrated, and the brown residue was purified by column chromatography (6 × 12 cm silica, 0.9 l of 2:1 hexane/EtOAc, followed by 1.5 l 1:2 hexane/EtOAc) to afford (I) (394 mg, 30%) and (II) (788 mg, 61%) as white solids. Compound (I) was recrystallized from EtOAc (m.p. 416–418 K). Data for (I): R_F 0.10 (1:1 hexane/EtOAc); $[\alpha]_D^{23}$ −7.6 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.29 (*d*, 1H, *J* = 2.6 Hz, C1—H), 4.60 (*dd*, 1H, *J* = 1.8, 6.0 Hz, C4—H), 4.16 (*dq*, 1H, *J* = 1.8, 7.0 Hz, C5—H), 3.50 (*s*, 3H, OCH_3), 3.46 (*dd*, 1H, *J* = 4.9, 6.0 Hz, C3—H), 3.04 (*dd*, 1H, *J* = 2.6, 4.9 Hz, C2—H), 1.32 (*d*, 3 H, *J* = 7.0 Hz, C6—H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 163.7 (C═O), 93.5 (C-1), 72.9 (C-4), 70.9 (C-5), 56.5 (OCH_3), 43.3 (C-2), 40.3 (C-3), 14.6 (C-6); HRMS (ESI) *m*/*z* calculated for $[C_8H_{11}NO_4]Na^+$: 208.0580; found: 208.0572.

Crystal data

$C_8H_{11}NO_4$	Z = 4
M_r = 185.18	D_x = 1.405 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 5.7376 (6) Å	μ = 0.11 mm^{-1}
b = 9.3890 (9) Å	T = 193 (2) K
c = 16.2562 (16) Å	Prism, colorless
V = 875.73 (15) Å^3	0.62 × 0.30 × 0.25 mm

Data collection

Bruker SMART 1000 CCD area detector/PLATFORM diffractometer	6970 measured reflections 1076 independent reflections 1014 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.022
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	θ_{max} = 26.4°
T_{min} = 0.746, T_{max} = 0.972	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.1153P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.082	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
1076 reflections	
118 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.412 (2)	N—C3	1.476 (2)
O1—C5	1.440 (2)	N—C8	1.419 (2)
O2—C1	1.4020 (19)	C1—C2	1.501 (3)
O2—C7	1.429 (3)	C2—C3	1.473 (3)
O3—C4	1.458 (2)	C3—C4	1.517 (2)
O3—C8	1.349 (2)	C4—C5	1.510 (2)
O4—C8	1.198 (3)	C5—C6	1.513 (3)
N—C2	1.502 (2)		
C1—O1—C5	117.39 (14)	N—C3—C2	61.25 (12)
C1—O2—C7	112.94 (16)	N—C3—C4	105.93 (15)
C4—O3—C8	108.86 (12)	C2—C3—C4	115.00 (15)
C2—N—C3	59.27 (12)	O3—C4—C3	103.42 (14)
C2—N—C8	116.57 (14)	O3—C4—C5	107.56 (15)
C3—N—C8	105.90 (13)	C3—C4—C5	112.02 (15)
O1—C1—O2	113.19 (15)	O1—C5—C4	107.71 (13)
O1—C1—C2	114.15 (14)	O1—C5—C6	114.80 (14)
O2—C1—C2	104.54 (14)	C4—C5—C6	112.59 (16)
N—C2—C1	121.67 (15)	O3—C8—O4	123.09 (16)
N—C2—C3	59.47 (11)	O3—C8—N	111.25 (15)
C1—C2—C3	120.81 (15)	O4—C8—N	125.41 (16)

In the absence of significant anomalous dispersion effects, Freidel pairs were merged and the absolute configuration was assigned

arbitrarily. H atoms were placed in idealized positions (C—H = 0.98–1.00 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(parent atom).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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